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with Sulfur Hexafluoride**

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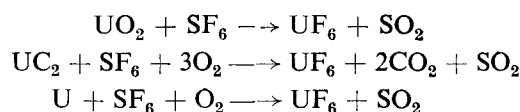
REPROCESSING OF NUCLEAR FUELS BY FLUORIDE VOLATILIZATION WITH SULFUR HEXAFLUORIDE

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ABSTRACT

A new procedure was developed for the reprocessing of nuclear fuels by fluoride volatilization, based on the fact that uranium or other uranium containing fuels can be fluorinated in a single step to uranium hexafluoride with sulfur hexafluoride at temperatures above 800° C. The essential reactions taking place can be represented by the following equations :



Advantageous for the use of sulfur hexafluoride is its property to be non-corrosive up to temperatures of about 500° C.

In order to perform the process, the fuels are first pulverized in a known manner and then fluorinated either with pure sulfur hexafluoride alone or together with oxidation agents like oxygen, air, manganese dioxide or others. The fluorination can be done in two steps. At first the starting material is fluorinated at temperatures between 700° C and 800° C, separating the non volatile uranyl fluoride from the easily volatile fission product fluorides. Afterwards, in the second step the UO_2F_2 is transformed to the easily volatile UF_6 at about 900° C.

For the reprocessing of coated particle containing fuels it has proved appropriate, either to crack and pulverize these particles prior to fluorination or to treat them at temperatures of about 900° C up to 1100° C with oxygen or a mixture of oxygen and sulfur hexafluoride, eventually in the presence of combustion catalysts. The fluorination can be achieved using either the fluidized bed or the conventional rotating oven technique. As constructing material for the ovens, besides others; especially pure alumina has stood the test.

The advantages of the new procedure are not only its simplicity and economy, another important fact is the absolute unotoxicity of sulfur hexafluoride. It does not act corrosive on any part of the gas inlet system. Small amounts of fluorine contained in the off-gas stream may be reconverted into sulfur hexafluoride by reaction with sulfur. This adds another advantage of re-using the so formed sulfur hexafluoride. A required high factor of decontamination of the formed uranium hexafluoride may be achieved applying the known absorption-desorption technique on sodium fluoride columns.

1. — INTRODUCTION

A basic question affecting the economics of nuclear power reactor is the selection of a suitable process for the regeneration of nuclear fuels. It is to be expected

that most of the power reactors shall be carbide, metal, or oxide fueled. An unequivocal choice however, as to which type might be the best is as yet impossible. Special attention is required for the reprocessing of nuclear fuels containing coated particles, which are regarded to be the most promising fuel type for high temperature gas-cooled reactors. It should well be suited to reprocessing by volatilization, particularly if a separation of fissile and fertile material is desired.

The reprocessing of the graphite fuel element balls of the Jülich AVR-reactor necessitates either a modification of the known aqueous or non aqueous procedures, or the development of a new process especially suited for the pyrolytic carbon coated fuel particles. For some time we have been investigating in our laboratory the possibility of reprocessing such fuels using a combined combustion-fluorination process.

It is a well established opinion that the fluoride volatilization should be able to compete with, or even to displace some day the aqueous regeneration procedures. This statement is based on the facts that :

- (a) a higher degree of decontamination can be achieved using smaller volumes;
- (b) smaller expenditures for installations are necessary due to fewer process steps;
- (c) one obtains directly-concentrated waste residues;
- (d) criticality dangers are decreased, since perilous concentration aggregations can hardly occur throughout all process steps, and finally
- (e) the problem of radiation damage of chemicals is unimportant.

In addition, the volatile uranium hexafluoride end-product, present the advantage of being directly introducible into an isotope enrichment cascade.

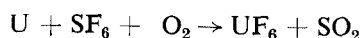
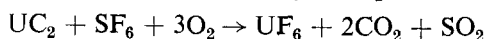
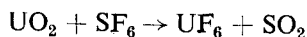
The transformation of uranium hexafluoride into the oxide, carbide, or metal presents no insurmountable technical difficulties.

It has been established that fluoride volatilization will be likewise suitable to all three separation problems in reactor technology, namely :

- 1. the separation of plutonium, natural uranium and fission products,
- 2. the separation of enriched uranium-235, fission products, and alloying metals, and
- 3. the separation of thorium, protactinium, and uranium.

2. — THE SULFUR HEXAFLUORIDE PROCESS

A new procedure was developed for the reprocessing of nuclear fuels by fluoride volatilization, based on the fact that uranium or other uranium containing fuels can be fluorinated in a single step to uranium hexafluoride with sulfur hexafluoride at temperatures above 800° C. The essential reactions taking place can be represented by the following equations :



Advantageous for the use of sulfur hexafluoride is its property of being non-corrosive up to temperatures of about 500° C.

In order to perform the process, the fuels are first pulverized in a known manner and then fluorinated either with pure sulfur hexafluoride alone, or together with oxidation agents like oxygen, air, manganese dioxide or others. The fluorination can be done in two steps. In the first, the starting material is fluorinated at temperatures between 750° C and 800° C, separating the non-volatile uranyl fluoride from the easily-volatile fission product fluorides. Afterwards in the second step, the UO_2F_2 is transformed to the easily-volatile UF_6 at about 900° C. In case it is unnecessary to get the high degree of decontamination for the uranium hexafluoride obtained hereby, the fluorination reaction can be performed in a single step under suitable conditions at temperatures between 850° C and 900° C. Care has to be taken that the fluorine concentration is high enough in the reaction zone to avoid the production of uranium fluoride intermediates. For the reprocessing of coated particle-containing fuels it has proved appropriate either to crack and pulverize these particles prior to fluorination, or to treat them at temperatures of about 900° C up to 1100° C with oxygen or a mixture of oxygen and sulfur hexafluoride, eventually in the presence of combustion catalysts.

The fluorination can be achieved using either the fluidized bed or the conventional rotating oven technique. The best materials for the ovens appear to be especially pure alumina. The fluidized bed technique presents several advantages for the realization of the process, since the equipment does not require any moving parts.

The reaction zone of the oven must be coated with pure alumina, fluorspar, or other fluorine resistant materials. For agitating the fluidized bed nitrogen or air is used. In this new process, removal of the heat of reaction is no where near as big a problem as in the case of using fluorine gas, since the heat of formation for the fluorination of UO_2 with SF_6 , for example, is much smaller than for F_2 . The values of ΔH_{298} are — 60.96 kcal/mole and — 252 kcal/mole, respectively. The question of whether the fluorination with sulfur hexafluoride is also possible in molten salts is not, as yet, completely solved. One of the main difficulties are corrosion problems.

The advantages of this new procedure lie not only in its simplicity and economy, but also in the absolute non-toxicity of sulfur hexafluoride. It does not react corrosively on any part of the gas inlet system. Small amounts of fluorine contained in the off-gas stream may be reconverted into sulfur hexafluoride by reaction with sulfur, thus adding another advantage. A high factor of decontamination of the resulting uranium hexafluoride may be achieved by applying the absorption-desorption technique on sodium fluoride columns.

3. — FLOWSHEET OF THE SULFUR HEXAFLUORIDE PROCESS

A tentative schematic flowsheet for the processing of uranium-containing fuel with sulfur hexafluoride is shown in Fig. 1.

The nuclear fuel is first chopped and pulverised, then stored in a storage container. The total usable volume of the container must be smaller than would contain

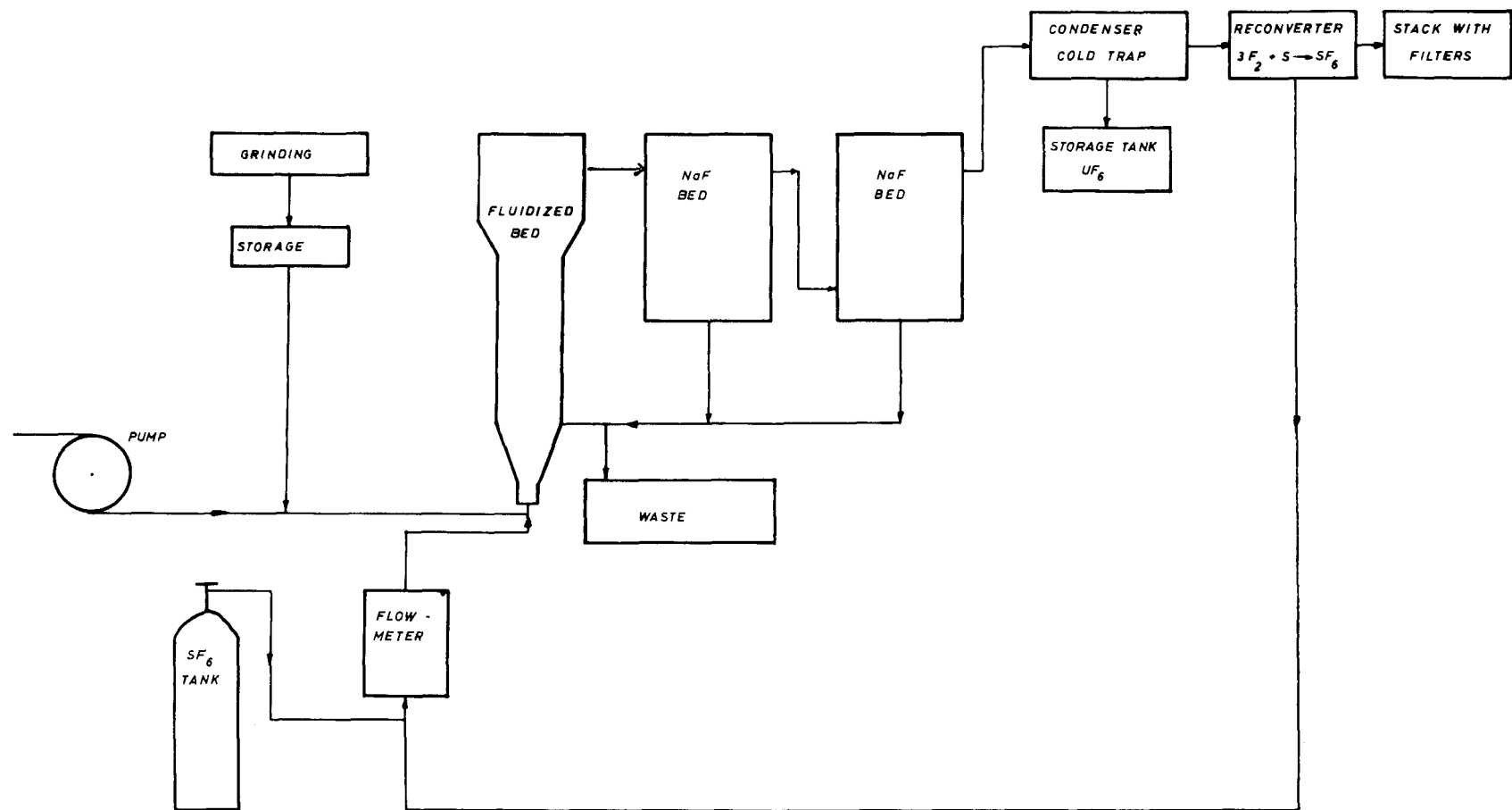


Fig. 1. — Schematic flowsheet of the Sulfur Hexafluoride process.

a critical mass. Using a transport pump and a nitrogen (or air) stream, the pulverized material is fed into the fluidized bed oven together with sulfur hexafluoride. The addition of SF_6 from the storage tank is monitored by observing a flowmeter. The reaction zone of the oven is heated up to about 900°C either by induction or resistance heating.

On top of the furnace the volatile UF_6 thus formed is released and absorbed on a sodium fluoride column. By raising the temperature of the NaF -bed, the UF_6 is desorbed and may be deposited in a cold trap and stored in a special tank. A second sodium fluoride bed is used for additional fission product decontamination. The waste from the process is removed batchwise, and might be poured into cans or long pipes and capped for storage. Fluorine gas which did not react in the fluorinator is reconverted into SF_6 by reaction with sulfur at elevated temperature and may be re-utilized.

4. — FURTHER DEVELOPMENT

So far, most of the work has been done on a scale of a few grams in cold runs only, with and without the addition of fission. It was thus possible to gather information on the behaviour of certain important fission products. We are pursuing our initial investigations along three lines :

1. Fluorination of uranium-containing materials with SF_6 in a fluidized bed,
2. Fluorination of uranium-containing materials with SF_6 in a rotating oven, and
3. Fluorination of uranium-containing materials with SF_6 in molten fluoride salts.

The capacity of the different fluorination devices is approximately one hundred grams of uranium. Before starting with highly-irradiated material, we still need much more information from cold runs, especially concerning yields of the different products, reaction mechanisms involved, and construction material problems.

The fluorination with sulfur hexafluoride in a packed bed seems to be more promising than a fluidized one, since here the gas flow is much smaller. This would facilitate the decontamination of the otherwise-arising large amounts of waste gases. Because the heat of formation for SF_6 is markedly less than that of the reaction with fluorine, the risk of caking of the powder is not very big. It can be overcome by mixing the ground uranium-bearing fuel with coarse-grained inert material. The same argument goes for the application of the otherwise-over-used rotating oven. Our present experimental results confirm this supposition. Best results in the fluorination of UF_4 to UF_6 with fluorine were obtained using eutectic mixtures of molten fluoride salts. Whereas the difficult construction material and corrosion problems are fairly well solved using elementary fluorine for the fluorination in molten salts, this is not yet true for SF_6 .

Finally, our investigations include the absorption and desorption of UF_6 on NaF -beds and the reversion of UF_6 to UO_2 , using either hydrolysis with water vapor or decomposition in molten salts.